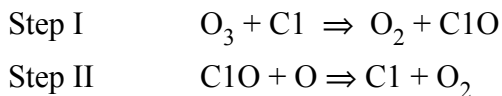


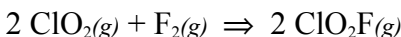
KINETICS

1. An environmental concern is the depletion of O_3 in Earth's upper atmosphere, where O_3 is normally in equilibrium with O_2 and O . A proposed mechanism for the depletion of O_3 in the upper atmosphere is shown below.



- (a) Write a balanced equation for the overall reaction represented by Step I and Step II above.
- (b) Clearly identify the catalyst in the mechanism above. Justify your answer.
- (c) Clearly identify the intermediate in the mechanism above. Justify your answer.
- (d) If the rate law for the overall reaction is found to be, $rate = k[O_3][Cl]$, determine the following.
 - (i) The overall order of the reaction
 - (ii) Appropriate units for the rate constant, k .
 - (iii) The rate-determining step of the reaction, along with justification for your answer.

2.

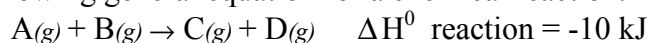


The following results were obtained when the reaction represented above was studied at $25^\circ C$.

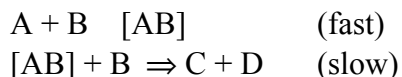
Experiment	Initial $[ClO_2]$, ($mol L^{-1}$)	Initial $[F_2]$, ($mol L^{-1}$)	Initial Rate of Increase of $[ClO_2F]$, ($mol L^{-1} sec^{-1}$)
1	0.010	0.10	2.4×10^{-3}
2	0.010	0.40	9.6×10^{-3}
3	0.020	0.20	9.6×10^{-3}

- (a) Write the rate law expression for the reaction above.
- (b) Calculate the numerical value of the rate constant and specify the units.
- (c) In experiment 2, what is the initial rate of decrease of $[F_2]$?
- (d) Which of the following reaction mechanisms is consistent with the rate law developed in (a). Justify your choice.
 - I. $ClO_2 + F_2 \rightarrow ClO_2F_2$ (fast)
 $ClO_2F_2 \Rightarrow ClO_2F + F$ (slow)
 $ClO_2 + F \Rightarrow ClO_2F$ (fast)
 - II. $F_2 \Rightarrow 2 F$ (slow)
 $2 (ClO_2 + F \Rightarrow ClO_2F)$ (fast)

3. Consider the following general equation for a chemical reaction.



- Describe the two factors that determine whether a collision between molecules of A and B results in a reaction.
- How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.
- Write the rate law expression that would result if the reaction proceeded by the mechanism shown below.



- Explain why a catalyst increases the rate of a reaction but does not change the value of the equilibrium constant for that reaction.

4. Graphical methods are frequently used to analyze data and obtain desired quantities.

- (a) $2 \text{ HI}(g) \Rightarrow \text{H}_2(g) + \text{I}_2(g)$

The following data give the value of the rate constant at various temperatures for the gas phase reaction above.

T (K)	<i>k</i> (litre/mol sec)
647	8.58×10^{-5}
666	2.19×10^{-4}
683	5.11×10^{-4}
700	1.17×10^{-3}
716	2.50×10^{-3}

Describe, without doing any calculations, how a graphical method can be used to obtain the activation energy for this reaction.

- (b) $A(g) \Rightarrow B(g) + C(g)$

The following data give the partial pressure of A as a function of time and were obtained at 100°C for the reaction above.

P_A (mm Hg)	<i>t</i> (sec)
348	0
247	600
185	1200
105	2400
58	3600

Describe, without doing any calculations, how graphs can be used to determine whether this reaction is first or second order in A and how these graphs are used to determine the rate constant.